The Permanence to Acid Deterioration of Vegetable Leather Retanned with Alum

By R. W. FREY, *Senior Chemist*, and C. W. BEEBE, *Associate Chemist*

It has been shown in previous studies[1,2] that marked resistance to acid deterioration may be imparted to vegetable tanned leather by retanning with chrome to an extent that does not alter materially the characteristics of a vegetable tannage. This has been found to be invariably true with leathers experimentally tanned in the laboratory, without dyeing and finishing. Frequently, however, completely finished commercial leathers of a vegetable-chrome retannage have not shown the degree of permanence to be expected.

Because of an apparent analogy between chrome and alum tannages, it would seem probable that a similar effect might be obtained by an alum retannage of vegetable tanned leather. The substitution of aluminum salts for those of chrome suggests several possible advantages, including availability from domestic sources and at a lower cost in some cases, and elimination of a bluish or greenish cast that frequently is quite apparent and objectionable. A further advantage might lie in a preferred mordanting action at times of alum as an aid in dyeing and finishing.

So far as the authors are aware, alum retannage has not been used in practice. On a laboratory scale no difficulties have been encountered up to the present in retanning with alum. The leather produced is of good quality and does not differ appreciably in appearance and feel from vegetable tanned leather.

For a study of the comparative permanence of alum retanned leather, as shown by exposure in the gas chamber, a set of leathers was tanned in the laboratory. Pieces from the bend area of a three-ounce, full grain cowhide split, previously limed, unhaired, washed, and preserved in borophenol solution, were tanned in a liquor made from equal proportions of chestnut wood extract and sulfited quebracho extract, to a degree of tannage close to 55. After being vegetable tanned the pieces were divided into five lots so as to be directly comparable as regards position in the hide. Two lots were retanned with alum to contain, respectively, around 1.5 per cent and 3 per cent of Al_2O_3. Two lots were likewise retanned with chrome to contain, respectively, about 1.5 per cent and 3 per cent Cr_2O_3. The other lot was left without further treatment to serve as the vegetable tanned control for comparison.

For the alum retannage there was used a stock liquor of aluminum sulfate, neutralized one-fourth with sodium carbonate, and containing

sodium chloride equal to the amount of aluminum sulfate present. For the chrome retannage, a stock liquor of chrome alum neutralized one-third with sodium carbonate was used. The aluminum sulfate and chrome alum liquors were not heated during or after addition of the sodium carbonate. They were allowed to stand, however, for at least three days before being used.

After retannage the leathers were washed and put into a dilute sodium bicarbonate bath until approximate equilibrium was reached at about pH 4.5. The leathers were then thoroughly washed, oiled lightly by hand on the grain and flesh sides with neatsfoot oil, and dried.

The significant data on the analyses of these leathers before exposure in the gas chamber are given in Table I.

TABLE I

ANALYSIS OF ORIGINAL LEATHERS

Tannage	Total ash*	Al_2O_3*	Cr_2O_3*	Soluble non-tannins*	Soluble tannin*	pH	Degree of tannage
	per cent	per cent	per cent	per cent	per cent		
Vegetable only.....	0.3			4.7	7.8	4.17	55
Vegetable plus alum.....	1.9	1.8		1.5	1.7	4.00	79
Vegetable plus alum.....	3.7	3.6		1.2	0.8	4.02	77
Vegetable plus chrome...	2.2		1.9	0.9	1.2	3.84	65
Vegetable plus chrome...	3.2		3.0	1.0	1.0	3.77	64

From each piece of leather uniform strips were cut, one immediately after the other. Alternate strips were placed for accelerated aging in the gas chamber, described recently[3], in which the pollution of the atmosphere is dependent upon the fumes from the burning of methyl alcohol containing amyl sulfite. The remaining strips were kept in a sealed jar to serve as unexposed controls. Ten strips were used for each test and each control. One set of strips for each leather was exposed for twelve weeks and another set for eighteen weeks. After exposure, the leathers including the controls were tested for tensile strength and analyzed for pH by the glass electrode, total sulfur by the bomb method, and soluble nitrogen obtained by extraction of the leather with water at 50° C. followed by extraction with 0.1*N* sodium carbonate solution at laboratory temperature. The per cent deterioration is expressed as the loss in tensile strength resulting from exposure in the gas chamber. The results of the physical tests and analysis are given in Table II.

Based upon loss in tensile strength, the alum retanned leathers show an exceptionally high degree of resistance to deterioration, being even significantly better in this respect than the chrome retanned leathers containing about the same amount of Cr_2O_3. The difference between the two retannages and the vegetable tanned leather is, of course, quite marked.

TABLE II

PHYSICAL AND CHEMICAL DATA ON UNEXPOSED AND EXPOSED LEATHERS

Tannage	Al_2O_3* or Cr_2O_3	Deterioration after exposure for 12 weeks	Deterioration after exposure for 18 weeks	pH values after exposure for 12 weeks	pH values after exposure for 18 weeks	Gain in sulfur as H_2SO_4 after exposure for 12 weeks†	Gain in sulfur as H_2SO_4 after exposure for 18 weeks†	Total soluble nitrogen after exposure for 12 weeks†	Total soluble nitrogen after exposure for 18 weeks†
	per cent	per cent	per cent			per cent	per cent	per cent	per cent
Vegetable only		42.2	59.1	2.40	2.20	2.34	2.84	2.54	3.28
Vegetable plus alum	1.8	11.1	22.4	3.33	3.09	1.68	2.17	0.20	0.84
Vegetable plus alum	3.6	5.3	16.7	3.57	3.39	2.71	2.98	0.10	0.23
Vegetable plus chrome	1.9	18.6	33.2	2.71	2.25	2.02	2.50	0.23	0.72
Vegetable plus chrome	3.0	12.1	25.3	2.77	2.22	2.33	2.85	0.20	0.45

*Expressed on basis of moisture-free leather.
†Expressed on basis of air-dry leather.

After eighteen weeks exposure in the gas chamber the vegetable tanned leather lost 59 per cent of its original strength, as compared to 33.2 per cent and 25.3 per cent for the chrome retanned leathers containing 1.9 per cent and 3.0 per cent, respectively, of Cr_2O_3, and only 11.1 per cent and 5.3 per cent for the alum retanned leathers containing 1.8 per cent and 3.6 per cent, respectively, of Al_2O_3. In other words, at the end of eighteen weeks the vegetable tanned leather suffered a loss in strength of over twice as much as the more resistant of the two chrome retanned leathers and three and one-half times as much as the corresponding alum retanned leather.

The data from chemical analysis are quite in harmony with the results from the physical tests. The leathers of both retannages show much lower soluble nitrogen values after exposure. The high pH values of the alum retanned leathers are quite outstanding. It is of particular significance that even after 18 weeks' exposure the pH values of these leathers were still above 3.

For purposes of comparison, similar sets of all the leathers were exposed in the old model gas chamber[4], used in previous studies of the permanence of leathers. The pollution of the atmosphere of this chamber depends on the oxides of sulfur formed upon the combustion of illuminating gas. There were no significant differences in the effects produced by the two chambers. Consequently, the results gotten with the chamber used formerly have not been included.

The studies just described must be considered as preliminary. They deal for the time being only with comparative permanence as reflected by accelerated aging in the gas chamber. A number of interesting and perhaps valuable possibilities are suggested by an analogous application of alum retanning to other types of leather, such as upholstery, shoe upper, bag, sole, and belting. Further exploration of the possible merits of this retannage is planned.

Summary

No references have been found to the application in practice of an alum retannage of vegetable tanned leather. It is suggested that such a process may possess a number of advantages over the similar use of chrome. Compounds of aluminum are readily available from domestic sources. Aluminum salts used for tanning do not produce the bluish to greenish undertones often resulting from the use of chrome.

Alum retannage of vegetable tanned leather produces an effect similar to chrome retannage in imparting to the leather marked resistance to acid rot.

The protection resulting from a given Al_2O_3 content of the leather appears to be appreciably greater than that from the same quantity of Cr_2O_3.

Judged by the basic vegetable tannage used in these studies, the appearance of undyed, unfinished alum retanned leather is superior in color to chrome retanned leather in a corresponding condition.

There is need of more information on the properties imparted to vegetable tanned leather by retanning with alum. A further study of alum retanning, particularly in its application to different types of vegetable tanned leathers, such as upholstery, shoe upper, bag, sole, and belting, is planned to determine the possibilities in this direction.